Optimization of ion trap parameters for the analysis of dilute samples in the presence of an interfering matrix

Analysis of polychlorinated biphenyls in transformer oil

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ABSTRACT

The analysis of dilute samples in the presence of an interfering matrix was improved by optimizing the operating parameters of an ion trap in a GC–ion trap system. For a mixture of nine polychlorinated biphenyls (PCBs) in 1% transformer oil, two strategies were successfully employed to increase signal-to-noise (S/N) ratios. By limiting the mass range scanned to those m/z values that include most of the ion fragments due to PCBs and increasing the number of microscans per scan in this regime, S/N values were increased by a factor of 1.5. Further improvements in S/N by up to a factor of ten are achieved by raising the radio frequency (rf) storage level so that low molecular weight ions due to the transformer oil are not stored. An upper limit on how high the rf storage level can be adjusted is determined by the storage efficiency of the ion trap which decreases at high rf storage levels. Ion dissociation is also a limiting factor at high rf storage levels. Best detection limits for five of the nine PCBs studied were obtained when the rf storage level was tuned to $m/z = 74$, a regime where most of the transformer oil ions are no longer stored.

INTRODUCTION

Techniques for environmental analysis often depend on the ability to identify and quantitate trace amounts of analyte in the midst of the interfering matrix. Often the properties of the matrix are such that signals from the matrix overlap with those of the analyte and the inherent sensitivity of a particular technique toward the compound of interest is diminished. Because most analytical techniques are geared toward samples with interferences, it is often necessary to perform sample cleanup procedures prior to analysis. The process is time consuming and extra handling may result in some sample loss. Consequently, there is much interest in developing techniques where analytes in complicated matrices can be analyzed without prior sample manipulation.

Another complication of environmental analyses is that not all components of a mixture are of regulatory interest or highly toxic. Usually only a few components of a mixture pose an environmental hazard and it is important to have some way of quickly and reliably determining if these species are present. Mass spectrometers are useful detectors in this regard, and GC–mass spectrometry systems have become popular anlytical techniques because of their sensitivity, dependability, and universal response toward organic compounds. Tandem mass spectrometry (MS–MS) detectors are useful for increased sensitivity towards analytes in interfering matrices [1], although the overall sensitivity is reduced.

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The application of an ion trap mass spectrometer to environmental analyses is very promising. Among the attractive features are the low detection limits that result from trapping ions in a confined space and the population build-up that results. Mixture analysis capabilities are possible with an ion trap using it in a MS–MS mode [2]. In addition, some work has been done to determine if the ion trap can be optimized for trace analyte detection without resorting to MS–MS [3–5], which would be desirable because of the higher sensitivity of the analysis as well as the library searchability of the resulting electron impact mass spectra.

We were interested in studying the operating conditions of the ion trap mass spectrometer to elucidate which parameters could be adjusted to increase the analyte response in a background of an interfering matrix. The number of ions stored in an ion trap is a complicated function of the ionization time, the applied d.c. voltage ($V_{d.c.}$), the rf drive frequency (Ω) and the amplitude (V_{rf}) of the radio frequency (rf) voltage and the geometry of the ion trap (usually characterized in terms of the trap radius r). There is also great flexibility in setting the range of masses scanned in the ion trap so that only selected mass ranges or even selected ions can be scanned. Unfortunately many of these parameters are interrelated, so that they can not be optimized independently. In addition, there are limits as to how far from normal operating conditions some parameters can be tuned before good mass spectra are no longer obtained. For example, simply increasing the ionization time so that more analyte ions are created can fill the trap with too many ions so that space–charge effects are a problem [6]. Clearly a systematic approach, based on the limits of stable operating conditions in an ion trap, needs to be developed to guide one in choosing which parameters to adjust so that the signal of a selected analyte ion in the midst of undesired background ions is enhanced.

We have chosen to investigate the detection and quantitation of polychlorinated biphenyls (PCBs) in transformer oil as an example of the analysis of trace components in a complex matrix. PCBs are present in the environment as mixtures of many of the 209 theoretically possible congeners and were widely used in electrical transformers, condensers and paints because of their thermal and chemical stability. However, it is the stability of PCBs combined with the toxic properties of some congeners that makes them so dangerous and their identification and quantitation critical. Mass spectrometers are useful for identifying which isomers are present but can be limited by the interferences from the matrix [7–9]. Extensive cleanup methods have been developed but are time consuming [10–12]. An optimized protocol for the analysis of dilute analytes in complex matrices using the ion trap without prior cleanup can be useful for PCB analysis.

EXPERIMENTAL

Sample preparation

The nine PCBs used are: 2,6-dichlorobiphenyl and 4,4'-dichlorobiphenyl (parent ion m/z 222); 2,2',6,6'-tetrachlorobiphenyl and 3,3',4,4'-tetrachlorobiphenyl (parent ion m/z 292); 2,2',4,4',6,6'-hexachlorobiphenyl and 3,3',4,4',5,5'-hexachlorobiphenyl (parent ion m/z 360); 2,2',3'3',5,5',6,6'-octachlorobiphenyl and 2,3,3',4,4',5,5',6-octachlorobiphenyl (parent ion m/z 430); and decachlorobiphenyl (parent ion m/z 500). All were obtained from Ultra Scientific (North Kingstown, RI, USA) as was the transformer oil. The nine PCB mixture was prepared in HPLC-grade hexane obtained from Aldrich (Milwaukee, WI, USA) and spiked with 1% (v/v) transfer oil. For the narrow mass range studies, the concentration of each PCB was 200 pg/μl; a more dilute solution of 50 pg/μl in each PCB was used for the studies in which the rf storage level was optimized. Octachloronaphthalene obtained from Ultra Scientific was used as an internal standard.

Ion trap conditions

All experiments were performed on a Saturn II GC–ion trap system using a septum-equipped programmable injector (SPI) manufactured by Varian Associates (Walnut Creek, CA, USA). No modifications were made to the instrument.

Electron impact ionization was used. Rf storage amplitudes were adjusted using the Saturn software; voltages corresponding to mass-to-charge ratios of 20, 46, 74, 102, 145, 153 and 160 were used. The range of masses scanned was adjusted in the acquisition method editor; individual settings are detailed in the section on narrow mass range scanning.

The automatic gain control (AGC) level was set to 30 000 and kept constant from run-to-run. The ionization time for each microscan is directly proportional to the AGC level setting and inversely proportional to the total number of ions detected in the trap during a 200 μs prescan. A computer algorithm is used to automatically adjust the ionization time of the microscan based on the number of ions detected in the trap during the prescan. If too many ions are present in the trap the ionization time for the microscan is reduced to keep the population of ions below a level where space charge effects would degrade resolution. Conversely, if very few ions are detected during the prescan, the ionization time is increased so that the population of ions is increased and sensitivity is improved. The maximum ionization time is 25 ms.

GC conditions

GC conditions for a DB-5 column with helium as the carrier gas were taken from ref. 13. The column was purchased from Varian (Sunnyvale, CA, USA) and was 30 m × 0.25 mm I.D. with a film thickness of 0.25 μm. The oven program used was as follows: 1 min at 80°C; 80–150°C at 4°C/min; 150–280°C at 2°C/min; and 6.5 min at 280°C. The injector program was 120–200°C at 120°C/min and then at 200°C for the duration of the analysis. The elution order of the PCBs along with their retention times were as follows: 2,6-dichlorobiphenyl (23.11 min); 4,4'-dichlorobiphenyl (29.43 min); 2,2',6,6'-tetrachlorobiphenyl (32.10 min); 2,2',4,4',6,6'-hexachlorobiphenyl (43.09 min); 3,3',4,4'-tetrachlorobiphenyl (47.09 min); 2,2',3,3',5,5',6,6'-octachlorobiphenyl (58.15 min); 3,3',4,4',5,5'-hexachlorobiphenyl (61.45 min); 2,3,3',4,4',5,5',6-octachlorobiphenyl (68.24 min) and decachlorobiphenyl (73.43 min).
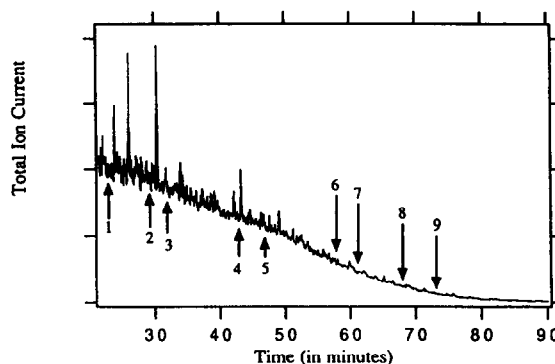

Fig. 1. Plot of total ion intensity as a function of time. Arrows point to the time at which the indicated PCB isomer elutes. Spikes in the chromatogram are due to column bleed.

RESULTS AND DISCUSSION

The difficulty of analyzing PCBs in transformer oil is demonstrated by the chromatogram shown in Fig. 1, where it can be seen that the PCB peaks are completely obscured by the coeluting transformer oil. Transformer oil is a mixture of aliphatic, alicyclic and polynuclear aromatic hydrocarbons with alkyl substituents [11] and some transformer oil components will have the same masses and boiling ranges as the PCBs. A mass spectrum of the transformer oil used in our studies is shown in Fig. 2. Very large signals from a typical hydrocarbon fragmentation pattern are seen for m/z values less than 130. At masses of interest for PCB analysis (m/z values
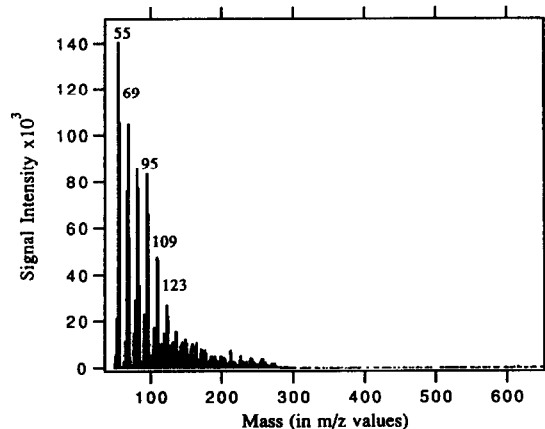

Fig. 2. Mass spectrum of a 1% transformer oil in hexane solution.

greater than 200), the signal intensities of the transformer oil fragments are considerably smaller than at low masses.

Because most of the transformer oil mass fragments are grouped in a low mass regime, two strategies for optimizing the PCB signal can be investigated. In one, the mass range scanned by the instrument is limited to the mass range of the parent PCB ion; most of the transformer oil ions will not be included in the scan. This technique will be referred to as narrow mass range scanning. The other strategy will be to raise the rf storage level so that low mass ions due to transformer oil are not stored in the ion trap and then filling the ion trap with more PCB ions by increasing the ionization time.

Narrow mass range scanning

A full mass range scan in the Saturn ion trap typically has the endpoints of m/z 50 and 650. When acquiring data at the rate of 1 s/scan, the instrument is actually performing three micro-scans per scan. The three microscans are averaged to produce the final scan recorded at that time in the chromatographic analysis.

In a narrow mass range scan, only a limited range of masses is scanned. For the analysis of PCBs in transformer oil, the range of mass scanned includes the parent PCB peak as well as some of the major fragments. For 2,6-dichlorobiphenyl, the mass range scanned was m/z 145–265; the number of microscans per scan rose to eight. A chromatogram run using full mass range scanning and displayed in the single ion monitoring mode of m/z 222 produces a peak for 2,6-dichlorobiphenyl with $S/N = 6.5$. The same sample run under narrow mass range conditions results in a peak with $S/N = 9.5$. A library search identified the peak as a dichlorobiphenyl even though only m/z values between 145 and 265 were available. The Saturn software allows for different mass ranges in different segments of a chromatogram and it was possible to do customized narrow mass range scans for each of the nine PCBs. Scans included the parent ion as well as fragments up to 70 m/z values less. Improvements in S/N were seen for all PCBs using narrow mass range scanning and matches were made to library mass spectra.

Increasing the number of microscans per scan increases the number of signal measurements that are averaged for the recorded scan. Based on a statistical analysis, the increase in the S/N value should be proportional to the square root of the ratio of the number of microscans per scan using narrow mass range scanning to the number of microscans per scan using full mass range scanning. In the example described above, the expected increase was a factor of 1.6 which is fairly close to the observed improvement of 1.45. It seems reasonable to assume that by limiting the mass range scan to an even more narrow mass range that further improvements in S/N should occur. A very narrow mass range scan of m/z 210 to 230 was run on the dichlorobiphenyl sample. The number of microscans per scan jumped to 20 and the expected improvement was a factor of 2.6. However, the observed improvement was only 1.7 which is not much better than using a narrow mass range scan. The observed deviation from the predicted behavior may be due to the non-random nature of the noise source; the major contribution to the background is from transformer oil ions at the same m/z as the PCB ion of interest.

Raising the rf storage level

The amplitude of the rf storage voltage (V_{rf}) determines the lower mass limit of which ions are stored in the ion trap. The relationship between V_{rf} and the stability parameter q_z is a complicated function based on the solutions to the Mathieu equation of ion motion in an oscillating electric field. For a conventional ion trap with the endcaps grounded, a radius of 1 cm and operating at 1 MHz, q_z is related to the ion mass (m), the charge on the ion (z) and V_{rf} as follows [14].

$$q_z = \frac{0.0978 V_{rf}}{m/z} \qquad (1)$$

Ions with q_z values greater than 0.908 do not have stable trajectories and exit from the ion trap. Under normal operating conditions, the amplitude of the storage voltage is chosen so that all ions with m/z values greater than 20 are stored in the ion trap. By increasing the amplitude of V_{rf}, the q_z value for an ion of a given
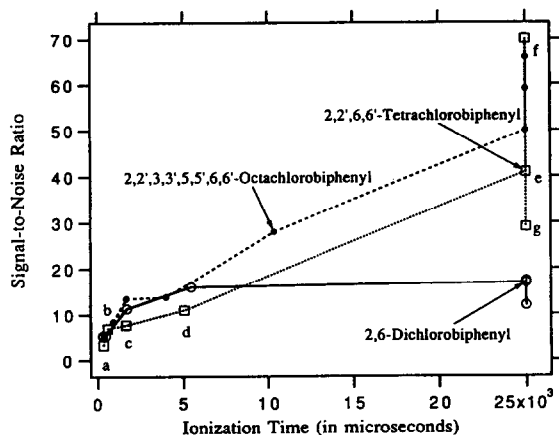
Fig. 3. S/N values as a function of ionization time. The lower case letters at each point correspond to the storage level used to generate the recorded ionization time. Mass-to-charge ratios are: (a) 20, (b) 46, (c) 74, (d) 102, (e) 145, (f) 153 and (g) 160.

mass increases and when q_z becomes greater than 0.908, the ion assumes an unstable trajectory and is not stored. Lower mass ions reach the point of instability before higher mass ions as V_{rf} is increased.

For the PCB sample in transformer oil, raising the rf storage level eliminates many of the lower molecular weight transformer oil ions from the trap. Since the ion trap has a fixed capacity for the total number of ions that can be stored before space-charge repulsion is a problem, a decrease in the number of low-molecular-mass ions trapped allows for the storage of more higher-molecular-mass PCB ions. The ionization time is increased so that more ions are created. Since the transformer oil fragments are the major background source, the increase in the number of PCB ions relative to transformer oil ions trapped should lead to an increase in S/N.

To demonstrate the benefit of the increased ionization time made possible by raising the rf storage level, the PCB in transformer oil sample was analyzed with the rf storage level set to one of the following m/z values: 20, 46, 74, 102, 145, 153 or 160. Narrow mass range scanning of at least 70 m/z values was used for each PCB. S/N ratios for the parent PCB ions and ionization times were measured for each PCB at each rf storage level. As shown in Fig. 3, a substantial improvement in the S/N values for each of the PCBs is observed as the ionization time increases. For octachlorobiphenyl, the increase in S/N was from 9 (measured when the ionization time was less than one thousand microseconds) to 70 (measured when the ionization time was at 25 ms). (There is some variation in S/N values at 25 ms because N is very small, often only 2, 3 or 4 counts.) S/N values measured at the default storage level of m/z 20 and best S/N values for all nine PCBs are included in Table I.

S/N values may have been even greater at high rf storage levels had there not been loss of PCB parent ions due to fragmentation. It was

TABLE I

DETECTION LIMITS AND S/N VALUES FOR NINE PCBs AT DEFAULT AND OPTIMUM SETTINGS

Compound	Detection limit at m/z 20 (in pg/μl)	Best detection limit (in pg/μl)	Storage level	S/N at m/z 20	Best S/N	Storage level
2,6-Dichlorobiphenyl	48	8	74	5	17	102
4,4'-Dichlorobiphenyl	79	10	74	2	8	153
2,2',6,6'-Tetrachlorobiphenyl	10	5	145	3	60	153
3,3',4,4'-Tetrachlorobiphenyl	10	7	74	3	17	153
2,2',4,4',6,6'-Hexachlorobiphenyl	34	3	74	6	150	160
3,3',4,4',5,5'-Hexachlorobiphenyl	25	6	102	4	32	153
2,2',3,3',5,5',6,6'-Octachlorobiphenyl	50	1	74	9	70	160
2,3,3',4,4',5,5',6-Octachlorobiphenyl	41	4	46	10	43	145
Decachlorobiphenyl	40	6	46	30	140	102

possible to monitor the extent of PCB fragmentation as the rf storage level was increased by analyzing a PCB sample without transformer oil (so that interferences at similar m/z values are reduced) under full mass range scanning conditions. The observed dissociation pathway is the loss of two chlorine atoms. By monitoring the ratio of the PCB parent ion signal to the signal of the peak at an m/z value 70 lower, it was possible to record the extent of fragmentation at high rf levels. Results for five of the PCBs are shown in Fig. 4.

All of the PCBs show decreases in the ratio of parent ion to fragment; for some it is expecially significant. 2,3-Dichlorobiphenyl, 2,2',6,6'-tetrachlorobiphenyl, 2,2',4,4',6,6'-hexachlorobiphenyl and 2,2',3,3',5,5',6,6'-octachlorobiphenyl have fragmentation ratios that decline by more than 40% at high rf storage levels. The behavior of the dichlorobiphenyl fragmentation ratio is somewhat bizarre; it increases as the rf storage level is increased from m/z 102 to 145. More than likely this behavior is due to the instability of the m/z 152 fragment at a storage level corresponding to m/z 145. The other five PCBs do not have such extensive fragmentation.

An important and more universal factor leading to the loss of ion signal at high rf storage levels is the decrease in storage efficiency of the

ion trap at high rf storage levels. While the proportion of sample ion relative to matrix ions increases at higher rf levels, the total number of ions stored in the trap declines. The variations in trapping efficiency are demonstrated by monitoring the signal intensities of five fragment ions from perfluorotributyl amine as the rf storage level is increased. (Perfluorotributylamine is used for mass calibration and is introduced into the ion trap at a constant pressure through a separate inlet system.) The ionization time was held constant so that the same number of ions were created at each of the different rf storage levels studied. The results are shown in Fig. 5.

The number of perfluorotributylamine ions stored decreases once the rf storage level is increased beyond m/z 50 or 60. For the perfluorotributylamine fragments at m/z 69 and 131, the signal intensity drops to zero at the rf storage levels above the corresponding m/z value. The ion fragments at m/z 264, 414 and 614 all show a monotonic decrease from m/z 60 to 160. For a PCB analysis, the decrease in storage efficiency at higher rf storage levels counteracts the benefits obtained by the concomitant increase in ionization time. At some rf storage level, there will be an optimum regime for the analysis of the PCBs in transformer oil matrix.

The detection limits for all PCBs were measured at each of seven different rf storage levels.
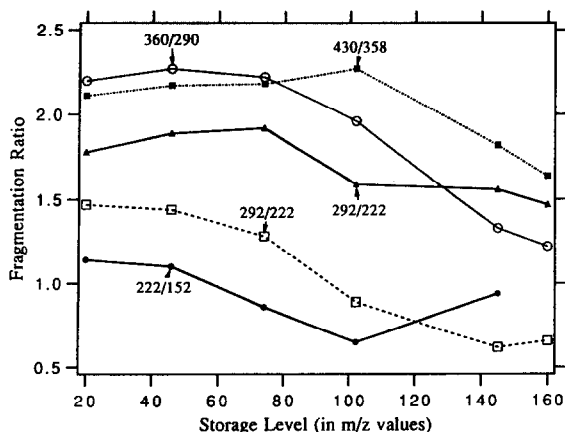

Fig. 4. Fragmentation ratio of five PCBs plotted as a function of rf storage level setting. ● = 2,6-Dichlorobiphenyl; □ = 2,2',6,6'-tetrachlorobiphenyl; ▲ = 3,3',4,4'-tetrachlorobiphenyl; ○ = 2,2',4,4',6,6'-hexachlorobiphenyl; ■ = 2,3,3', 4,4',5,5',6-octachlorobiphenyl.
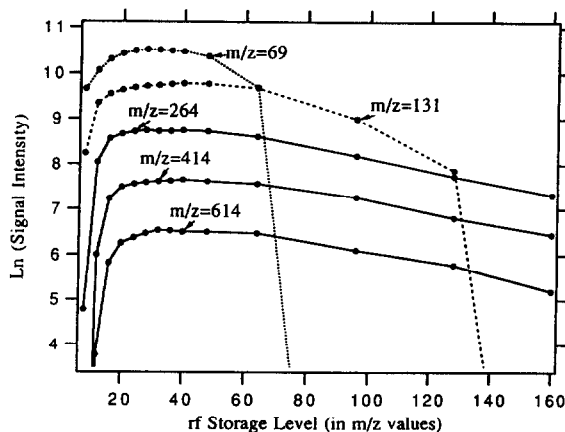

Fig. 5. Signal intensities of perfluorotributyl amine fragment ions as a function of rf storage level. The ionization time was held constant at 1.2 ms.

The calculation of detection limits is based on an EPA-suggested method [13]. The detection limits were determined by analyzing the PCB mixture at each rf setting three times, calculating the standard deviation for each compound from the three runs and then multiplying the standard deviation by 4.3. Optimum detection limits for each of the nine PCBs are included in Table I as well as the detection limits obtained at the default storage level of m/z 20. Best detection limits were measured at a storage level setting of m/z 74 for both dichlorobiphenyl isomers, 3,3',4,4'-tetrachlorobiphenyl, 2,2',4,4',6,6'-hexachlorobiphenyl and 2,2'3,3',5,5'6,6'-octachlorobiphenyl. For eight PCBs, optimum settings were between m/z values of 46 and 102, storage levels where a significant number of transformer oil ions were excluded from the trap and where the storage efficiency of the trap was still high. The optimum detection limits obtained using our protocol are comparable with those reported using a GC–electron-capture detection system [13].

CONCLUSIONS

We have outlined two strategies for improving the analysis of dilute samples in a transformer oil matrix. Narrow mass range scanning can be used to improve S/N ratios by a factor of 1.5 as compared to a full mass range scan. Raising the rf storage level so that low molecular weight matrix ions are not stored leads to an increase in S/N by nearly a factor of 10. Optimum detection limits were measured in a regime where the increase in signal intensity resulting from increased ionization times dominated over the loss in trapping efficiency at high rf storage levels.

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